

The impact and retention of spray droplets on a horizontal hydrophobic surface

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ABSTRACT

Spray retention, i.e. the overall capture of spray droplets by plants on initial or subsequent
impact, and after loss due to run-off, is an important stage in the spray application process as
droplet losses may result in reduced efficacy, economic loss, and environmental
contamination. The aim of this exploratory study is to determine whether a new method based
on calculating the volumetric proportions per impact type, i.e. adhesion, rebound and shatter,
can be used to predict spray retention. These volumetric proportions are calculated based on
logistic regression models, derived from vision-based droplet characteristics and impact
assessments, and laser-based spray characteristics. The advantages and limitations of such a

method are explored. The volumetric proportions per impact type on a horizontal, synthetic hydrophobic surface were determined for four different nozzles (XR 110 01 VS flat-fan nozzle, XR 110 04 VS flat-fan nozzle, XR 110 08 VS flat-fan nozzle and AI 110 08 VS air-induction nozzle) under controlled realistic conditions, and compared to the results of a retention test. The volumetric proportions of adhesion were much lower than the relative retentions, indicating that a considerable amount of rebound and shatter also contributed to final retention. The method should thus be improved by including the droplets retained after first impact and the retained proportions of partial droplet fragmentation but it is nevertheless considered a promising technique.

Keywords: spray retention, droplet impact, Weber number, volumetric proportion

Nomenclature

We	Weber number
ρ	liquid density (kg m^{-3})
\mathbf{u}	droplet velocity (m s^{-1})
d	droplet diameter (m)
σ	liquid surface tension (N m^{-1})
PTFE	polytetrafluoroethylene, Teflon [®]
PDPA	Phase Doppler Particle Analyser
θ_0	static contact angle ($^\circ$)
θ_{adv}	advancing contact angle ($^\circ$)
θ_{rec}	receding contact angle ($^\circ$)
BSF	Brilliant Sulfo Flavine
$We_{A/R}$	Weber number of transition between adhesion and rebound

51 $We_{R/S}$ Weber number of transition between rebound and shatter
52 $\Delta\theta$ contact angle hysteresis ($^{\circ}$)

53

54 **1. Introduction**

55

56 Efficient and sustainable crop protection requires that the various stages in the spray
57 application process are performed optimally and without detrimental effects on subsequent
58 stages (Forster, Mercer, Schou, 2012). These stages are (1) *deposition* (the amount impacting
59 the target area, i.e. application volume minus drift), (2) *retention* (the amount of spray
60 droplets captured by plants on initial or subsequent impact, after loss due to run-off), (3)
61 *uptake* (the fraction of retained material taken up into the plant foliage), and (4) *translocation*
62 (the amount of absorbed material translocated from absorption site to site of biological
63 activity) (Forster et al., 2012; Forster, Steele, Gaskin, Zabkiewicz, 2004). Poor efficiency in
64 any stage may result in economic losses, environmental contamination, food safety issues or
65 reduced biological efficacy (Reichard, Cooper, Bukovac, Fox, 1998; Zabkiewicz, 2007). This
66 paper will focus on the process of retention.

67 When a droplet impacts on a surface, three outcomes are possible: (1) *adhesion*, (2)
68 *rebound* or (3) *shatter*. When a droplet hits a surface, the kinetic energy of the droplet,
69 defined by its mass and velocity, causes it to spread out across the surface. The droplet
70 reaches its maximum spread when all the available kinetic energy is converted to potential
71 energy. Simultaneously, the contact angle of the droplet decreases from being advancing to
72 receding. Subsequently, the droplet will recoil due to surface tension. During both the
73 spreading and recoiling phases the droplet loses energy. If the energy losses are low enough
74 the droplet will bounce off the leaf. If the losses are too great then insufficient energy remains
75 for rebound and the droplet adheres (Forster et al., 2012; Spillman, 1984). If a droplet hits the

surface in a highly energetic state surface tension can be insufficient to maintain its integrity and it can shatter into finer droplets (Bergeron, 2003; Durickovic & Varland, 2005; Mercer et al., 2007). For optimal spray retention, droplets that impact the plant surface must remain on the plant and thus the volume percentage of adhering droplets should be maximised (Boukhalfa, Massinon, Belhamra, Lebeau, 2014; Massinon & Lebeau, 2013).

The type of impact outcome depends on the characteristics of the liquid (surface tension, viscosity), droplet (size, velocity) and surface (roughness, wettability, orientation). Each impact event can be characterised by a Weber number ($We = \rho |\mathbf{u}|^2 d / \sigma$) which represents the ratio between kinetic energy and surface energy of the droplet, where ρ (kg m^{-3}), \mathbf{u} (m s^{-1}), d (m) and σ (N m^{-1}) are respectively the liquid density, droplet velocity, droplet diameter and liquid surface tension. Rioboo, Voué, Vaillant, De Coninck (2008) proposed for a certain surface and in the absence of viscosity modifications, a constant critical Weber number for transition between impact outcomes. Based on droplet Weber numbers and impact outcomes, logistic regression models can be established which describe the probability of droplets to belong to each impact class according to their Weber number. For example, in the models, a droplet with critical Weber number would have an equal probability of belonging to one of two different impact classes (Massinon & Lebeau, 2012b). In combination with data on the droplet size and velocity spectra of a spray, the volumetric proportions of the spray in each impact class could be determined from these regression models.

The aim of this exploratory study was to determine whether a new method based on calculated volumetric proportions per impact type, i.e. adhesion, rebound and shatter, could be used to predict spray retention. These volumetric proportions are calculated based on logistic regression models, derived from vision-based measurements of droplet characteristics and impact assessments, and laser-based measurements of spray characteristics. The advantages and limitations of such a method are discussed. The development of such a method might

allow spray characteristics and settings that could result in improved retention on different crop surfaces to be identified without the need for time-consuming and costly retention studies. The surfaces of leaves vary widely in wettability, from superhydrophilic to superhydrophobic (Koch & Barthlott, 2009). However, difficult-to-wet leaves are of great concern in agriculture since they are difficult to treat with crop protection products. Hence, this study focuses on hydrophobic surfaces. Because of the variability inherent to natural leaf surfaces (Taylor, 2011), a synthetic hydrophobic surface is used to perform tests under controlled but realistic conditions.

2. Materials and methods

The study consisted of different steps which are described here but they will be discussed in more detail in the subsequent sections. Firstly, high-speed images of droplets of tap water impacting on horizontal, synthetic, hydrophobic PTFE coated slides were acquired for four different nozzle-pressure combinations as described by Massinon and Lebeau (2012b). Then, droplet size and velocity data were obtained using image analysis and the types of impact were visually assessed and classified into adhesion, rebound or shatter. From the droplet characteristics, Weber numbers were calculated. Subsequently, logistic regression models were developed with the impact outcomes adhesion and shatter as binary dependent variables, with droplet Weber numbers as independent variable. Based on these logistic regression models, the probability of a droplet to belonging to each impact class was established. From the probability distribution of the different impact outcomes, two critical Weber numbers of transition were determined. The droplet size and velocity characteristics of the whole spray were then determined using a PDPA laser for the same nozzles at 400 kPa and the volumetric proportions per impact type at this spray pressure were calculated from these spray

characteristics and the previously acquired logistic regression models. Finally, as a validation, a retention test on PTFE coated slides, using a chemical tracer, was performed using the same nozzle-pressure combinations. The relative retentions were compared with the volumetric proportions of adhesion.

2. 1. Surface characteristics

A PTFE coated microscope slide (72 mm x 24 mm; part number X2XES2013BMNZ, Thermo Fisher Scientific Inc., Waltham, MA, USA) was used in the spray experiments to determine the volumetric proportions per impact type. The relevance of this type of synthetic surface as target surface was shown by Massinon & Lebeau (2012a) in a comparative study with outdoor grown wheat leaves and this type of surface was used here because it is possible to relate these results to a more practical situation. The static contact angle, θ_0 , was measured once on 10 different slides by the sessile drop method using Drop Shape Analysis system DSA14 and Drop Shape Analysis software (A.KRÜSS Optronic GmbH, Hamburg, Germany). The average static contact angle of distilled water on the slides was $139^\circ \pm 4.8^\circ$, indicating the hydrophobic nature of the surface ($90^\circ < \theta_0 < 150^\circ$) with a tendency towards superhydrophobicity ($150^\circ < \theta_0 < 180^\circ$) (Bhushan & Jung, 2011). However, the wettability found in this study greatly differed from that of the PTFE coated slides used by Massinon & Lebeau (2012b) which came from the same batch, i.e. $\theta_0 = 169^\circ$. These differences may be because of different measuring methods, or damage or unwanted contamination of the slides. Furthermore, some variation in θ_0 may be due to the intrinsic heterogeneity of the surfaces as contact angle can occur in a range of values between the advancing contact angle, θ_{adv} , and the receding contact angle, θ_{rec} (Bhushan & Jung, 2011).

2. 2. *Spray droplet impact events and characteristics*

In this exploratory study, droplet size, velocity and impact type for a total 419 impacting droplets generated using four different nozzle-pressure combinations (Table 1), i.e. a TeeJet XR 110 01 extended-range flat-fan nozzle at 400 kPa, a TeeJet XR 110 04 extended-range flat-fan nozzle at 300 kPa, a TeeJet XR 110 08 extended-range flat-fan nozzle at 240 kPa and a TeeJet AI 110 08 air-induction flat-fan nozzle at 290 kPa (TeeJet Technologies, Wheaton, IL), were measured using a dynamic spray application bench (Fig. 1) as described previously (Massinon & Lebeau, 2012b). All nozzles were made from stainless steel with VisiFlo® color-coding. The nozzle-pressure combinations were chosen to represent the wide range of droplet sizes and velocities found in the field but were restricted to limited pressure at higher flow rates due to the capacity of the spray bench. Every nozzle-pressure combination was tested twice. For every repetition a new PTFE coated slide was used.

Tap water was used in the experiments. The surface tension of the tap water was determined by the Particle and Interfacial Technology Group, Ghent University using the Wilhelmy plate method which measures the downward force exerted on a platinum plate of known size, hanging vertically from a microbalance (Sartorius AX423, Sartorius AG, Goettingen, Germany), when the plate is brought in contact with the liquid. Prior to the measurements, all materials were submerged in a concentrated acid solution overnight to remove possible residues and then rinsed thoroughly with distilled water. The measurements were repeated three times. The surface tension of tap water was $0.071 \pm 0.000 \text{ N m}^{-1}$.

Drops were generated by a single nozzle mounted 500 mm above the horizontally positioned target slide which was located below the centre of the spray. A linear displacement stage, actuated by a servomotor, moved the nozzle at a forward speed of 2 m s^{-1} perpendicular to the camera-lighting axis. Drop impact events were recorded using a high-speed camera (Y4

CMOS, Integrated Design Tools, Tallahassee, FL, USA) and LED backlighting (19-LED Constellation, Integrated Design Tools, Tallahassee, FL, USA). The acquisition frequency was set at 20,000 images per second. The pixel size was calibrated by taking a picture of a graduated ruler and by counting the number of pixels for a given length. The spatial resolution of the optical system was $10.8 \mu\text{m pixel}^{-1}$. The size of the image was about 2 mm high by 11 mm long.

Droplet sizes and velocities were determined from the acquired images by image analysis using Motion Studio (Integrated Design Tools, Tallahassee, FL, USA). Two images of each measured droplet just before impact were selected. Droplet diameter was calculated from the circle corresponding to the area of the droplet. Droplet velocity was determined by the difference in the position of the bottom of the droplet in the two selected frames divided by the elapsed time. Both droplet diameter and velocity were converted from pixels to μm by multiplication by the spatial resolution of the optical system. Only droplets that were in focus were measured. Droplets were considered to be in focus when the peripheral blur width was less than 4 pixels ($< 45 \mu\text{m}$). The blur width was determined based on the intensity of the pixels at the expected edge of the droplet compared to a fixed threshold of the 8-bit greyscale image. In addition, images of each impact event were visually assessed and classified in one of the three impact classes, i.e. adhesion, rebound or shatter. Using the droplet size and velocity, the droplet Weber numbers were computed.

2. 3. Logistic regression models, Weber numbers of transition, and volumetric proportions per impact type

Logistic regressions (Lammertyn, Aerts, Verlinden, Schotsmans, Nicolai, 2000) were performed with the impact classes adhesion and shatter as binary dependent variables, and

droplet Weber number as independent variable, using SPSS Statistics 19 (SPSS Inc. 2010, IBM corporation, New York, USA). Probability distributions for adhesion and shatter were determined for a range of Weber numbers (0.001 to 10,000) using

$$P_k = \frac{1}{1+e^{-\text{logit}_k}} = \frac{1}{1+e^{-\alpha_k-\beta_k We}} \quad (1)$$

where k is the type of impact outcome (adhesion or shatter), α_k is the intercept of the k^{th} logit, and β_k is the regression coefficient of the k^{th} logit. For rebound, the probability distribution was calculated for the range of Weber numbers by subtracting their probability for adhesion and shatter from 1. The intersection between Weber number probability distributions of the different impact outcomes was defined as the critical Weber number which determines the transition between impact types. In the log-log graphs of velocity versus diameter, a constant Weber number of transition corresponds to a straight line with a -0.5 slope (Rioboo, Voué, Vaillant, De Coninck, 2008).

Droplet size and velocity spectra of the whole spray of the same nozzles at a spray pressure of 400 kPa were obtained using a PDPA laser-based measuring set-up also at 500 mm below the nozzle as described by Nuyttens, Baetens, De Schampheleire, and Sonck (2007). The volumetric proportions of the spray in each impact class for every nozzle operated at 400 kPa were calculated from the spray droplet characteristics and the probability of the spray droplets to belong to an impact class based on their Weber numbers, the acquired logistic regression models, and Eq. (1).

2. 4. Retention tests

Spray retention was evaluated by a fluorimetric method using Brilliant Sulfo Flavine (BSF) as chemical tracer at a targeted concentration of 5.0 g l⁻¹. The surface tension of the spray liquid was determined as described above (0.057 ± 0.000 N m⁻¹). Spray applications

were performed using a greenhouse sprayer (Delvano, Harelbeke, Belgium) and a three-nozzle spray boom mounted on a spray track (Foqué & Nuyttens, 2011). The three-nozzle set-up was necessary to provide a uniform distribution with known application rates in the area of interest. The distance between the nozzles on the spray boom was 500 mm. The nozzles were located 500 mm above the collectors which were located in the centre of the spray boom. A total of three collector types were used in the experiments. In addition to measurements on PTFE coated slides, control measurements were performed using discs from filter paper with a diameter of 30 mm and Petri dishes with a diameter of 35 mm filled with 3 ml of water. For each collector type, five samples were placed in a horizontal position, either by placing them in a clip (PTFE coated slides and filter paper) or on a wooden holder (Petri dishes filled with water). All collectors were positioned 50 mm above a rolling bench to avoid deposition of droplets rebounding on the bench. To avoid deposition on the underside of the collectors, filter papers of same size were attached to this side of the collectors. Collectors of the same type were positioned 52 mm apart and were located in the middle of the spray swath. The three collector types were placed behind each other in the direction of the moving spray boom. Applications were made at a spray pressure of 400 kPa and driving speed of 1.1 m s^{-1} resulting in application rates of 135 l ha^{-1} , 546 l ha^{-1} and 1095 l ha^{-1} for the XR 110 01 VS, XR 110 04 VS, and XR 110 08 VS and AI 110 08 VS nozzles, respectively. For every nozzle, three repetitions were performed with the same nozzle set. For every repetition, new collectors were used.

After exposure to the spray, the tracer was rinsed off the collectors in Petri dishes with 3 ml of water for the filter papers and 20 ml for the PTFE coated slides. Per sample, including the Petri dish collectors filled with water, 200 μl was analysed using a fluorimeter (Fluostar Optima, BMG Labtech GmbH, Offenburg, Germany, excitation filter 440 nm, emission filter 510 nm).

Statistical analyses were performed using IBM SPSS Statistics 19 (SPSS Inc. 2010, IBM Corporation, New York, USA). A two-way ANOVA with nozzle type and collector type and their interaction as fixed factors was performed on the relative retentions, i.e. the retentions relative to the theoretical applied spray volume. If significant, Tukey's post-hoc tests were performed.

3. Results and discussion

3. 1. Logistic regression models, Weber numbers of transition, and volumetric proportions per impact type

The logistic regression models for adhesion and shatter (Table 2), based on the 419 visually-assessed impacting droplets, fitted the data to an acceptable level (Hosmer-Lemeshow goodness of fit $P > 0.05$) and showed a relatively good association between the calculated Weber numbers and the observed droplet impact events (Nagelkerke $R^2 = 0.69$ and 0.94 , respectively). In total, 87.6% of adhesion and 99.0% of shatter events were classified correctly by the respective regression models. However, these models were built and assessed using the same data of the 419 impacting droplets, therefore one might expect a reasonably good fit. Despite the high R^2 value, the correlation does not give information on the predictive value of the model in this case but it gives a useful insight into the appropriateness of the method in general, which was the objective of the study. In particular, assuming that the impact events were classified correctly, R^2 deviating from 1 indicates errors in Weber numbers or unexplained variation due to, for example, variations in surface characteristics. The errors in Weber numbers may be explained by measurement errors in droplet diameter, velocity or surface tension. Using automated image processing analysis to determine the

droplet characteristics, as developed by Massinon and Lebeau (2012b), might help to increase objectivity and reduce measurement errors. Furthermore, we assumed that the surface characteristics were the same for all the PTFE coated slides, but due to surface heterogeneity the contact angles may have been different within slides (Bhushan & Jung, 2011) and the surface characteristics may also have differed between slides as every slide was only used once. Also, the static contact angle measurements were performed on slides not used in the experiments. In addition, during the spray experiments the PTFE coated slides became wet and droplets unavoidably impacted on both dry and wet surfaces. These variations in surface characteristics could have resulted in different impact behaviours for droplets with the same characteristics, thus influencing the association between the calculated Weber numbers and the observed droplet impact events. The logistic regression models could be improved by including surface characteristics, thus also improving the method to predict spray retention using volumetric proportions per impact type determined based on these models and laser-based spray characteristics in general. Including surface characteristics in the models could also extend the use of the method to other surfaces than PTFE coated slides, albeit this would not be a necessity when determining volumetric proportions for every surface separately.

The probability distribution of the different impact outcomes on the PTFE coated slides for a range of Weber numbers (0.001 to 10,000) is presented in Fig. 2. Figure 3 illustrates the droplet characteristics of the 419 visually-assessed impacting droplets. The Weber numbers of transition between adhesion and rebound ($We_{A/R} = 0.1$) and between rebound and shatter ($We_{R/S} = 98$) are outlined on both graphs. Higher values of We resulted in rebound and shatter of the impacting drop. Rioboo et al. (2008) reported $We_{A/R} = 0.2$ and $We_{R/S} = 60$ on superhydrophobic polypropylene surfaces ($\theta_0 = 150^\circ$) with Milli-Q water and Massinon and Lebeau (2012b) found $We_{A/R} = 0.3$, 0.3 and 0.4 , and $We_{R/S} = 70$, 60 and 50 on superhydrophobic PTFE coated slides ($\theta_0 = 169^\circ$) for distilled water (0.072 N m^{-1}) at spray

pressures of 200, 300 and 400 kPa, respectively. According to the authors of the latter study, differences in Weber numbers of transition are not pressure dependent but originate from the small number of drops they observed when We was close to the Weber number of transition. Despite the lower θ_0 of the PTFE coated slides used in this study, the value of $We_{A/R}$ here was somewhat lower compared to previous studies. Contact angle measurements are the main method to characterise the wettability of surfaces. As the contact angle increases, droplets are less likely to adhere to the surface (Bertola, 2008; Forster et al., 2012; Mercer et al., 2007). On surfaces with a low contact angle droplets tend to spread while high contact angles describe surfaces on which droplets form spherical shapes and the contact between the adhering droplet and the surface is small (Koch & Barthlott, 2009). On surfaces with high contact angles energy is dissipated more slowly, leading to increased energy on recoil and subsequent rebound (Mao, Kuhn, Tran, 1997). As discussed by Rioboo et al. (2008), variation in contact angle hysteresis ($\Delta\theta = \theta_{adv} - \theta_{rec}$), which is a measure for energy dissipation during the flow of a droplet over a solid surface (Bhushan & Jung, 2011), may explain the lower $We_{A/R}$ found in this study as the contact angle, contact angle hysteresis and Weber numbers of transition may differ locally owing to surface heterogeneity and can thus be higher or lower than those reported in the different studies. Nevertheless, θ_{adv} and θ_{rec} were not determined in this study so the effect of $\Delta\theta$ on the Weber numbers of transition cannot be confirmed.

The volumetric proportions within each impact class for the different nozzles at 400 kPa, calculated based on the logistic regression models and the measured droplet size and velocity characteristics of the spray, are presented in Table 3. In general, the volumetric proportions of adhesion were low for all nozzles ($\leq 2.8\%$) owing to the high contact angle and hydrophobic nature of the PTFE coated slides, as described above. A higher proportion of adhesion (13 %) was observed by Massinon and Lebeau (2012b) for distilled water using a TeeJet 110 03 nozzle at 400 kPa, corresponding with the larger $We_{A/R}$ found in that study. The slightly

different method of calculation applied by those authors, which did not include spray characterisation but only observations of impacts by high speed imaging of drops, may also have contributed to the larger volumetric proportions of adhesion.

Compared to the other nozzles used in this study, the XR 110 01 VS flat-fan nozzle gave the highest percentage of adhesion and rebound and the lowest percentage of shatter. Considerably lower proportions of adhesion and rebound and larger proportions of shatter were found for the other flat-fan nozzles (XR 110 04 VS and XR 110 08 VS). The air-induction nozzle AI 110 08 VS displayed the lowest proportion of adhesion and rebound, whereas the volumetric proportions of shatter were largest. Air-induction nozzles can produce sprays that contain droplets with inclusions of air when spraying a liquid with a reduced surface tension (Miller & Butler Ellis, 2000). These air inclusions are known to modify droplet impact behaviour, resulting in reduced rebound (Miller & Butler Ellis, 2000; Mota, Antuniassi, Chechetto, de Oliveira, Silva, 2013). The surface tension can be reduced by using a surfactant (Bergeron, 2003). With water alone, the proportion of air included in the spraying is very limited, even with air-induction nozzles (Mota et al., 2013). Furthermore, water-only droplets are assumed to lose their air inclusions by 200 mm below the nozzle (Butler Ellis et al., 2002). Therefore, Weber numbers and volumetric proportions per impact type were calculated in this study using tap water without correcting for possible air inclusion of the droplets produced with the air-induction nozzle. For the same reason, the logistic regression models were built without differentiating between flat-fan and air-induction nozzles. However, the presence of air inclusions may affect the impact behaviour, the density and consequently the Weber number when spraying other liquids. The extent of these effects will most likely depend on the proportion of air within individual droplets and future studies should aim to include a correction and determine whether flat-fan nozzles and air-induction nozzles should be considered separately. When for example an estimated amount of air of

20% is incorporated in the calculation of the Weber numbers of the droplets of the air-induction nozzle, based on the values reported by Faggion, Miller, and Butler Ellis (2006), both Weber numbers of individual droplets as Weber numbers of transition decreased, whereas volumetric proportions of adhesion remained similar, and those of rebound and shatter respectively slightly increased and decreased (data not shown).

The findings of the volumetric proportions per impact class can be explained by the droplet characteristics of the nozzles. A large amount of fine and slow moving droplets (Fig. 4 and 5), with consequently low kinetic energies and Weber numbers, is produced by the XR 110 01 VS flat-fan nozzle, resulting in a higher percentage of adhesion and a low percentage of shatter. Larger droplet size and velocity distribution spectra are generated by the XR 110 04 VS and XR 110 08 VS flat-fan nozzles, decreasing adhesion and increasing shatter. For the same nozzle size and spray pressure, the AI 110 08 VS air-induction nozzle produces bigger droplets, although with lower velocities for the same droplet size than the XR 110 08 VS flat-fan nozzle, in agreement with the findings by Nuyttens, De Schampheleire, Verboven, Brusselman, and Dekeyser (2009). This nozzle therefore produces much bigger droplets whose effect dominate, resulting in higher kinetic energies (data not shown), and favouring shatter.

3. 2. Retention tests

The results of the retention tests are presented in Fig. 6. The relative retentions were significantly influenced by the interaction between nozzle type and collector type ($P < 0.001$). The relative retentions of the control measurements (filter paper and Petri dishes filled with water) considerably differed from 100%, apart from the air-induction nozzle. The presence of air currents which mainly capture the fine droplets and prevent them from impacting on the

surface may partially account for this difference. The AI 110 08 VS air-induction nozzle produces large droplets which are less susceptible to air currents. Furthermore, large droplets are more likely to collide with the collector surface as they are less likely to deviate from their initial path when there are changes in the direction of air due to an object. By contrast, very small droplets follow almost exactly the streamlines of air flowing around an encountered object (Spillman, 1984). In addition, because of their higher velocity, coarse droplets are exposed to the influence of air movements for a shorter period than fine droplets (Matthews, 2000).

Due to the described effects of air currents, the relative retention on filter paper was significantly higher with the AI 110 08 VS air-induction nozzle than with the XR 110 01 VS flat-fan nozzle ($P = 0.005$). Furthermore, relative retention slightly increased with increasing nozzle size, although not significantly. With the Petri dishes filled with water the relative retention for the AI 110 08 VS air-induction nozzle significantly differed from all the standard flat-fan nozzles (XR 110 01 VS, XR 110 04 VS, XR 110 08 VS), whereas the retention values from the flat-fan nozzles did not differ from each other.

Unlike the other collector types, retention on the PTFE coated slides was significantly lower with the AI 110 08 VS air-induction nozzle than with the XR 110 01 VS flat-fan nozzle ($P = 0.036$) because of the higher kinetic energy of the droplets produced by the air-induction nozzle resulting in less adhesion on the hydrophobic surface.

Within the same nozzle type, the retentions on the PTFE coated slides were significantly lower than on the other collector types, except for the XR 110 01 VS flat-fan nozzle, whereas the other two collector types did not significantly differ from each other. These observations correlate with the lower wettability of the hydrophobic (PTFE coated slides) compared to the hydrophilic collectors (filter paper and Petri dishes filled with water). The absence of significant differences between the hydrophilic collectors suggests that the air flow around the

differently shaped collectors had little effect on the retention in this study, although the limited number of measurements per nozzle type per collector type ($n = 15$) may also conceal possible significant effects. In general, the XR 110 01 VS flat-fan nozzle shows fairly large and similar retentions ($\pm 75\%$) on both hydrophobic and hydrophilic collectors. On hydrophobic surfaces the best retention was obtained with the aforementioned nozzle type which produces fine and slow moving droplets that can easily adhere, whereas on hydrophilic surfaces even better retention was reached with larger nozzle sizes that produce coarser droplets which are less susceptible to air currents. Therefore, when selecting a nozzle type, the surface characteristics of the crop should be kept in mind as they highly affect retention. Nevertheless, the relative retentions obtained here were rather high, especially on the hydrophobic PTFE coated slides, most probably owing to the horizontal position of the collectors and the lower surface tension of BSF compared to normal tap water.

3. 3. Volumetric proportions per impact type versus retention tests

For every nozzle, the volumetric proportions of adherence measured on the PTFE coated slides (Table 3) were much lower compared to the relative retentions on this surface (Fig. 6). This indicates that besides adhering droplets a considerable amount of rebounding and shattering droplets were retained by the collector. This effect is probably more pronounced because of the horizontal collector position and the considerable size of the collectors. Future studies could therefore focus on performing retention studies with smaller surfaces, but more importantly the method should include droplets after first impact, and not merely adhering droplets, in order to determine retention based on the volumetric proportions per impact type. Crease, Hall, and Thacker (1991) and Mercer et al. (2007) already suggested that shattering is not necessarily a detrimental outcome as the smaller and slower-moving secondary droplets

426 that are produced may be captured on nearby leaf surfaces and it is not unlikely that those
427 secondary droplets could even be retained by the same surface, as mentioned by Massinon
428 and Lebeau (2013). The same argument can be advanced for rebounding droplets. Of course,
429 the droplets can also fall to the ground. Mercer et al. (2007) stated that if droplets bounce off
430 the surface completely, this generally happens at the first bounce as their energy is
431 substantially reduced by the initial impact. Tracking the droplets over a short additional
432 period of time may therefore considerably improve the method.

433 Furthermore, Boukhalfa et al. (2014) recently determined that a variable proportion of
434 partially fragmented droplets may be retained at the impact location and can account for a
435 considerable amount of retention (28-46 % on barley leaves). Future research should include
436 these forms of partial fragmentation to further improve the prediction of retention.

437 Some difference between volumetric proportions of adherence and relative retentions on
438 the PTFE coated slides may be due to a different methodology used in the two experiments.
439 As indicated above, the multiple nozzle set-up was a necessity to produce a uniform spray
440 distribution and known application rates so as to determine the relative retentions on the
441 collectors from different nozzle sizes. Also, a chemical tracer was needed to determine the
442 relative retentions. This tracer can however change the liquid characteristics and thus alter
443 impact behaviour. Future studies should therefore focus on using the same spray liquid in both
444 the tests to calculate volumetric proportions per impact type as well as the retention tests.
445 Moreover, for the same reason, when testing pesticides the right pesticide at the right
446 concentration for the application volume, should be used. Furthermore, compared to the
447 calculations of the volumetric proportions per impact type, which only used droplets that were
448 in focus and thus fell almost vertically, the retention tests consisted of a wider range of droplet
449 impact angles. Incorporating a 3D imaging system, such as presented by Dong, Zhu, and

Yang (2013), could provide an accurate measurement of droplet motion and help overcome these differences in methodology.

In addition, the energy and reflection angle of the rebounding and secondary droplets can influence retention. The image analysis of the method could be extended to measure diameter, velocity and reflection angle of the rebounding and secondary droplets. A 3D imaging system could furthermore improve information on the spreading of droplets and the direction of film breaking.

The proportion of droplets that finally remains on a plant surface depends on many factors including liquid surface tension and viscosity, surface roughness, wettability, angle and size, canopy structure and environmental conditions (Mercer et al., 2007). After optimisation, the method could be applied to investigate the effect of such reported liquid, surface and spray application characteristics, as suggested by Massinon and Lebeau (2012b).

In this study we used PTFE coated slides to assess the method using volumetric proportions per impact type to predict spray retention due to their reduced within-surface variability compared to natural leaf surfaces. Although many ways exist to construct surfaces with properties ranging from superhydrophilic to superhydrophobic (Sun, Feng, Gao, Jiang, 2005; Yan, Gao, Barthlott, 2011), artificial surfaces still differ from plant surfaces in their structure and chemistry, which may affect impact behaviour. Therefore, once optimised, the method should be applied in predicting spray retention on real leaves. Moreover, care should be taken that leaves of the correct species, developmental stage and growing conditions are used because these factors affect leaf surfaces (Butler Ellis, Webb, Western, 2004; Taylor, 2011). When conducting experiments on leaves a larger variation in droplet impact behaviour can be expected due to natural surface heterogeneity, as was found by Massinon and Lebeau (2012a).

Off course, besides the method to determine the volumetric proportions per impact type, the set-up of the retention test, which serves as reference, should be able to accurately determine spray retention under controlled, realistic and representative conditions in order to identify the effect of different spray and surface settings. For example, the EvaSprayViti developed by Codis et al. (2013), i.e. an adjustable, artificial vine that serves as test bench for assessing the agri-envirionmental performance of crop spraying equipment, might be a good reference. However, once completely optimised, the method suggested in this study, using volumetric proportions per impact type, could allow spray retention to be predicted and identify the most optimal spray settings for different crop surfaces without the need for the often more extensive and expensive retention studies.

Although the XR 110 01 VS flat-fan nozzle gave a significantly higher retention on the PTFE coated slides than the other nozzles (Fig. 6), corresponding with the volumetric proportions of adhesion (Table 3), the retentions of the other nozzles did not significantly differ from each other, while the results from Table 3 indicate considerably lower volumetric proportions of adhesion for the AI 110 08 VS air-induction nozzle. The absence of a significant difference in the retention test between the XR 110 08 VS flat-fan nozzle and the AI 110 08 VS air-induction nozzle is however in agreement with Cooper and Taylor (1999), who reported similar retention for flat-fan and air-induction nozzles with the same application rate on horizontal targets in still air conditions. The results from the retention test thus confirm that the method investigated here needs improvement before it allows ranking of the efficiency of application techniques with regards to spray retention.

According to Miller and Butler Ellis (2000), air-induction nozzles produce retention much closer to that of a fine spray. The higher application rate used with the AI 110 08 VS air-induction nozzle in this study may have caused significantly lower relative retentions with this nozzle than with the XR 110 01 VS flat-fan nozzle due to run-off and the altered

behaviour of impacting droplets on wetted surfaces. To allow comparison, future studies should be performed at the same application rates.

4. Conclusions

Retention tests were performed with the same nozzles (XR 110 01 VS flat-fan nozzle, XR 110 04 VS flat-fan nozzle, XR 110 08 VS flat-fan nozzle and AI 110 08 VS air-induction nozzle) at the same pressure (400 kPa) as to determine the volumetric proportions per impact type in order to assess if the volumetric proportions of adhesion could be used to predict retention. Based on this exploratory study several limitations of the method were identified and suggestions for improvement were given. It can be concluded that the volumetric proportions of adhesion on first impact alone are not enough to accurately predict retention and the method needs improvement before it allows ranking of the efficiency of application techniques regarding retention. Nevertheless, the method used is promising as it can be extended to measure other variables, such as diameter, velocity and reflection angle from rebounding and secondary droplets, needed to further improve retention models, which on their turn could be used to investigate the effects of different formulations, surface and spray application characteristics, without the need for time-consuming and costly retention studies.

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613
614
615

616 Table 1. Overview of tested nozzle-pressure combinations.

Nozzle type	Pressure (kPa)	Nominal Flow Rate (l min ⁻¹)
TeeJet ^a XR ^b 110 01 VS ^c	400	0.45
TeeJet XR 110 04 VS	300	1.58
TeeJet XR 110 08 VS	240	2.83
TeeJet AI ^d 110 08 VS	290	3.11

617 ^aTeeJet Technologies, Wheaton, IL

618 ^bExtended-range flat-fan nozzle

619 ^cStainless steel with VisiFlo[®] color-coding

620 ^dAir-induction flat-fan nozzle

621

622

623 Table 2. Logistic regression models for the impact outcomes adhesion and shatter, based on
 624 the 419 visually-assessed impacting droplets.

Impact class	Independent variable	β	SE	<i>P</i> -value
Adhesion	α	1.9	0.3	< 0.001
	We	-17.6	2.4	< 0.001
Shatter	α	-6.9	1.3	< 0.001
	We	0.1	0.0	< 0.001

625

Table 3. Volumetric proportions (%) of the impact outcomes (adhesion, rebound, shatter), calculated based on the logistic regression models and the measured droplet size and velocity characteristics of the spray, for different nozzles sprayed at 400 kPa and 500 mm height.

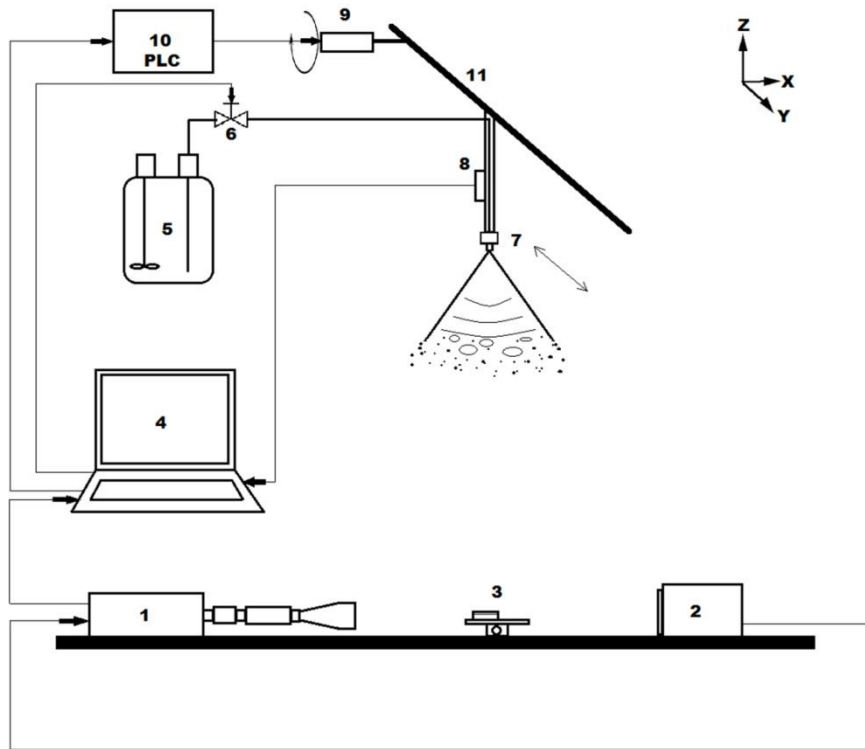
Nozzle type	Adhesion (vol.%)	Rebound (vol.%)	Shatter (vol.%)
TeeJet ^a XR ^b 110 01 VS ^c	2.8	92.2	5.0
TeeJet XR 110 04 VS	0.7	47.0	52.4
TeeJet XR 110 08 VS	0.6	49.6	49.8
TeeJet AI ^d 110 08 VS	0.1	21.6	78.4

^aTeeJet Technologies, Wheaton, IL

^bExtended-range flat-fan nozzle

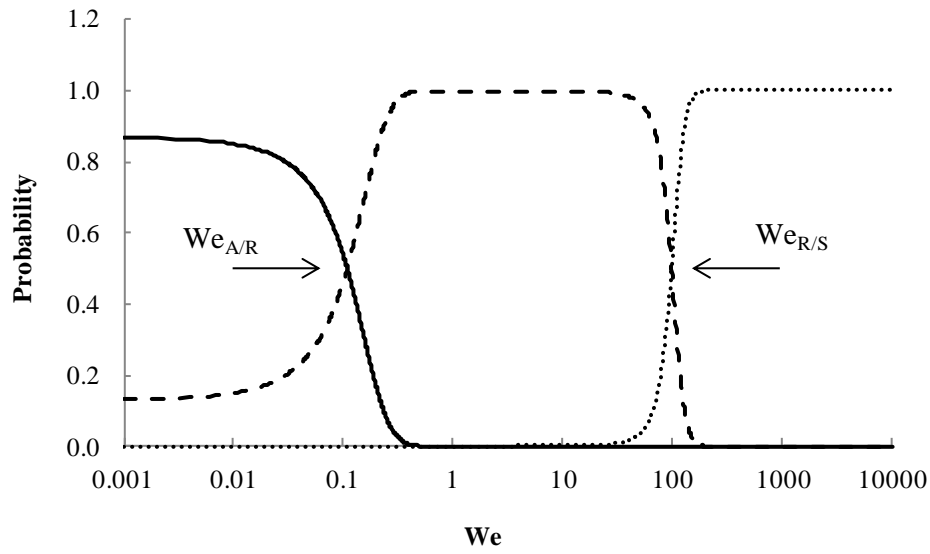
^cStainless steel with VisiFlo[®] color-coding

^dAir-induction flat-fan nozzle



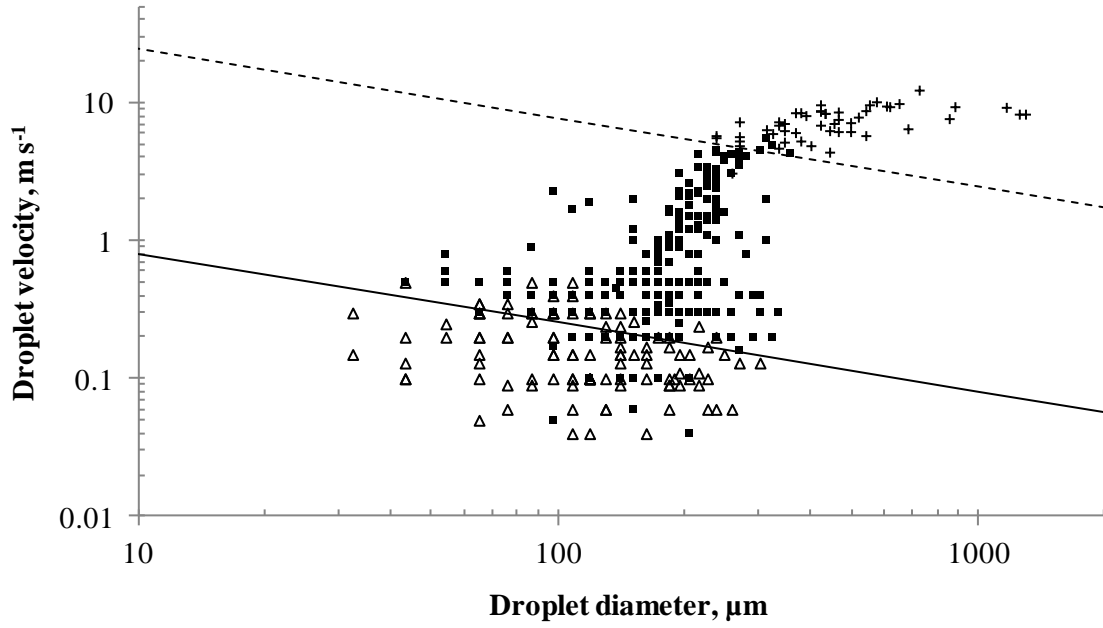
634

635 Fig. 1. Dynamic spray application bench: (1) high-speed camera, (2) LED lighting, (3) target
 636 surface on linear stage, (4) computer, (5) pressurised tank, (6) solenoid valve, (7) nozzle, (8)
 637 pressure gage, (9) servomotor, (10) programmable controller, (11) linear stage.



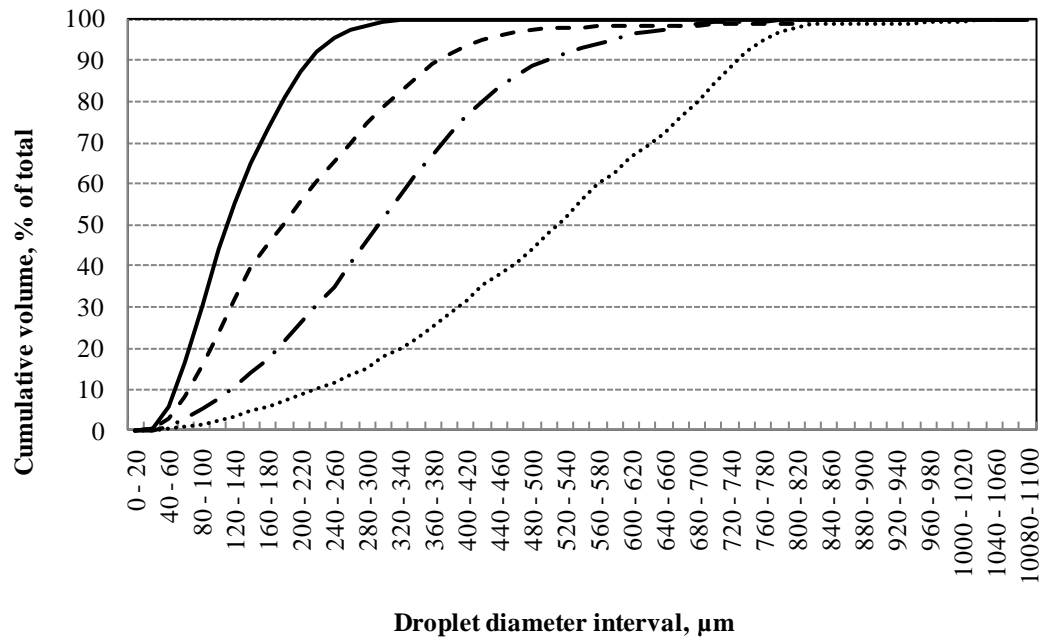
638

639 Fig 2. Probability distribution of different impact outcomes on the hydrophobic PTFE coated
 640 slide for a range of Weber numbers (0.001 to 10,000) obtained from logistic regression: —
 641 adhesion, --- rebound, ... shatter, $We_{A/R} = 0.1$, $We_{R/S} = 98$.



642

643 Fig 3. Impact outcomes on the hydrophobic PTFE coated slide of the 419 visually-assessed
 644 impacting droplets: Δ adhesion, \blacksquare rebound, $+$ shatter, — Weber number of transition between
 645 adhesion and rebound ($We_{A/R} = 0.1$), --- Weber number of transition between rebound and
 646 shatter ($We_{R/S} = 98$).



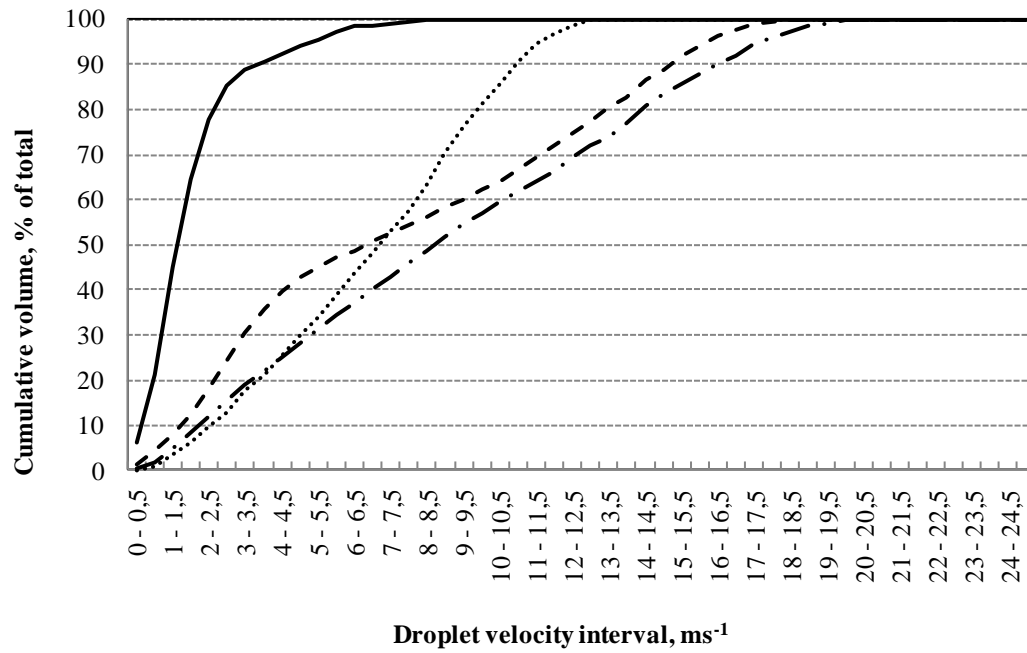
647

648 Fig. 4. Cumulative volumetric droplet size distribution for different nozzles at a pressure of

649 400 kPa: — TeeJet XR 110 01 VS flat-fan nozzle, ----- TeeJet XR 110 04 VS flat-fan

650 nozzle, - . - . - TeeJet XR 110 08 VS flat-fan nozzle, TeeJet AI 110 08 VS air-induction

651 nozzle.



652

653 Fig. 5. Cumulative volumetric droplet velocity distribution for different nozzles at a pressure
 654 of 400 kPa: — TeeJet XR 110 01 VS flat-fan nozzle, ----- TeeJet XR 110 04 VS flat-fan
 655 nozzle, TeeJet XR 110 08 VS flat-fan nozzle, TeeJet AI 110 08 VS air-induction
 656 nozzle.

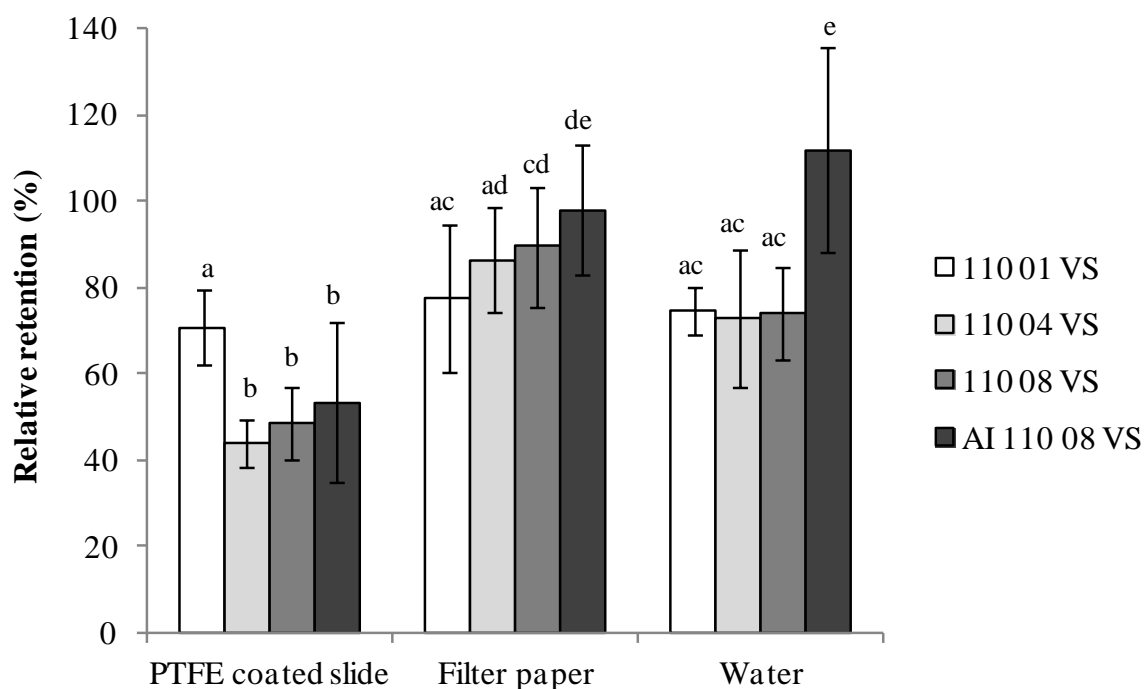


Fig. 6. Mean value and standard deviation of the retention of BSF relative to the theoretical applied volume (%) of the nozzles (TeeJet XR 110 01 VS flat-fan nozzle = white, TeeJet XR 110 04 VS flat-fan nozzle = light grey, TeeJet XR 110 08 VS flat-fan nozzle = dark grey, TeeJet AI 110 08 VS air-induction nozzle = black) on the different collectors (PTFE coated slides, Filter paper and Petri dishes filled with water). Different superscripts denote statistical significance at $P < 0.05$.